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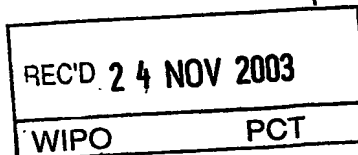
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**Patentanmeldung Nr. Patent application No. Demande de brevet n°**

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:  
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
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Nickel catalyst

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Title: Nickel catalyst

The invention relates to a catalyst comprising nickel, alumina magnesium and silica, to a method for preparing such a catalyst and to a process for hydrogenating unsaturated organic compounds.

Nickel/alumina catalysts with a nickel/aluminium ratio of 2-20 are  
5 known to be active catalysts for the hydrogenation of unsaturated organic compounds from EP-A 0 167 201. The catalysts claimed in EP-A 0 167 201 further comprise silica in a nickel/silica ratio of 1-20. The disclosed catalysts are prepared in a process wherein first a nickel hydroxide/carbonate is precipitated and thereafter aluminium nitrate and silicate are added. The  
10 resulting precipitate is thereafter activated with hydrogen. The examples show catalysts comprising at least 85 wt. % Ni that are used in the hydrogenation of fish oil. It is reported that they may retain their activity for a prolonged period and tend to show a high poison resistance. As an indication for selectivity an aspecific assay is referred to, based on a combination of melting point and  
15 hydrogenation time. Besides the fact that the latter parameter has been found to be rather an indicator for activity, no quantitative data are presented on the selectivity in soy bean oil hydrogenation though.

There is a continuing need for alternative catalysts for the hydrogenation of unsaturated organic compounds. In general when searching  
20 for a suitable catalyst for the hydrogenation of a particular compound, one has to compromise e.g. between activity and selectivity. For instance, certain catalyst characteristics (e.g. an open pore structure) may favour the selective hydrogenation of fatty oils while at the same time result in longer reaction times when hydrogenating more contaminated oils because of their higher  
25 susceptibility to poisoning. Therefore, often different types of catalysts are required for different types of unsaturated organic compounds. For example, a

catalyst may either be suitable for clean oils, such as soy bean oil, or for more contaminated oils, such as rape seed oil or fish oil.

It is an object of the present invention to provide a novel catalyst that may be used as a favourable alternative to known catalysts for  
5 hydrogenating unsaturated organic compounds, in particular fatty oils.

It has been found that this object can be realised by a catalyst comprising nickel, silica, alumina and also magnesium in a particular ratio.

Accordingly, the present invention relates to a catalyst comprising nickel, silica, alumina and magnesium, wherein the nickel to magnesium  
10 atomic ratio is 5-75, preferably 5-50.

In particular, the present invention relates to a catalyst comprising nickel, silica, alumina and magnesium, wherein the nickel to silicium atomic ratio (Ni/Si) is 2 to 30, the nickel to aluminium atomic ratio (Ni/Al) is 9 to 40 and the nickel to magnesium atomic ratio (Ni/Mg) is 5-75.

15 It has been found that a catalyst according to the present invention shows a very high activity for the hydrogenation of unsaturated compounds, in particular unsaturated fatty substances, such as fatty oils including unsaturated fats. The invention may very suitably be employed for the hydrogenation of fatty substances of vegetable and/or animal origin for food  
20 grade applications.

A catalyst according to the invention has been found to have a very high activity as a hydrogenation catalyst. In particular, a catalyst according to the invention is found to be highly active for relatively clean oils - i.e. oils with a relatively low sulphur content - like soy bean, as well as for more  
25 contaminated oils, like fish oil, having a high sulphur content.

The total weight percentage of Ni in the reduced catalyst may be chosen in a wide range, as defined by the Ni/Si, Ni/Al and Ni/Mg ranges. Preferably, the amount of nickel is at least 50 wt. % and not higher than 80 wt. %, more preferably the amount of nickel is 65-75 wt.%. Very good results  
30 have been achieved with an amount of nickel of 65-72 wt.%.

In a preferred embodiment, Ni/Si is about 2 to 22, more preferably about 2.5 to about 15. Very good results have been achieved with a Ni/Si of about 3 to about 7.5.

5 Ni/Al is preferably about 10 to about 35, more preferably about 10-30, even more preferably about 15-25. Very good results have been achieved with a catalyst having a Ni/Al of more than 20, e.g. up to 22.

Ni/Mg may preferably be chosen in the range of about 5-50, more preferably 5-30, even more preferably about 6 to about 20. Very suitable is a catalyst with a Ni/Mg of about 7.5-12.5, e.g. about 10.

10 In order to prevent oxidation of the catalyst it may be coated with a protective layer, such as a layer comprising a fatty substance. Very good results have been achieved with a catalyst coated with hardened soy bean fat. The physical characteristics of a catalyst may vary widely, inter alia depending upon the application.

15 The pore volume (as measured by N<sub>2</sub> desorption, 20-600 Å, on a Quantachrome Autosorb 6) may very suitably be chosen in the range of 0.4 to 1 ml/g. Preferably, the pore volume is about 0.55 to 0.75 ml/g, e.g. 0.6-0.7 ml/g.

Preferably, the catalyst has a volume average particle size (D(v,0.5)) of 3 to 8 µm. D(v,0.5), as used herein, is the value as measured by  
20 LASER diffraction with a Malvern MS 1002, lens 45 mm - which corresponds to a measuring range of 0.1-100 µm - using "Independent" as the model for calculating the particle size. Very good results have been achieved with a catalyst having a volume average particle size of about 4 to about 7 µm.

The nickel surface area is preferably 75 to 200 m<sup>2</sup>/g of nickel, more  
25 preferably approximately 100-175 m<sup>2</sup>/g of nickel, even more preferably approximately 100-150 m<sup>2</sup>/g of nickel. Very good results have been achieved with a catalyst having a nickel surface area of 110-145 m<sup>2</sup>/g of nickel. The nickel surface area as used herein is the value as can be determined by hydrogen chemisorption at 50 °C, after in-situ reduction with hydrogen (60  
30 ml/min) for 2 hours at 400 °C and subsequently degassing for 14 hours at 350

°C in a Carlo Erba Sorptomatic 1900. The amount of adsorbed hydrogen is determined by extrapolation of the reduction isotherm to zero pressure and the nickel surface area is calculated assuming a site density of  $6.77 \text{ \AA}^2/\text{atom}$ .

The BET surface area preferably is about 300 to about  $450 \text{ m}^2/\text{g}$  catalyst, more preferably about 350 to about  $400 \text{ m}^2/\text{g}$  catalyst. The BET surface area as used herein is the value that can be measured by determining the amount of nitrogen adsorbed at 77 K and  $P/P_0$  of approximately 0.3 and assuming a nitrogen cross sectional area of  $16.2 \text{ \AA}^2$ , after degassing the catalyst sample at 180 °C.

The average pore diameter (APD), as calculated from the measured pore volume (PV) and BET surface area by the formula  $\text{APD} = 40000 \cdot \text{PV} / \text{BET}$ , may for example very suitably be chosen in the range of about 10-500 Å, preferably in the range of about 40 - 200 Å, more preferably about 60 - 100 Å.

It is possible to make a catalyst in a process wherein first a nickel precipitate is made, which is subsequently aged with an alumina source and with a silica source (which may be added together with the alumina or thereafter).

In a preferred embodiment, the catalyst is made from a catalyst precursor that is prepared by co-precipitation, of which it will be clear to the skilled professional how to choose suitable method conditions. In a co-precipitation method according to the invention nickel, alumina, silica and magnesium are precipitated together (i.e. without forming intermediate precipitates of only one or some of the components). In such a method, a nickel source, a silica source, an alumina source and a magnesium source may be mixed in a liquid (e.g. water or an aqueous solution) to form a precipitate (a catalyst precursor), comprising all four said components.

Preferably the co-precipitation is carried out with the aid of a precipitant, e.g. an alkali metal carbonate (such as  $\text{Na}_2\text{CO}_3$ ) or an alkali metal hydroxide (such as  $\text{NaOH}$ )

It is an advantage of the above co-precipitation methodology that it can be performed in a single co-precipitation step.

Very good results have been achieved with a method wherein the co-precipitation is performed at alkaline pH, e.g. at a pH of approximately 7.5-8.5 (as measured at 25 °C). It has been found that under alkaline conditions a very efficient, generally a substantially complete precipitation of nickel and magnesium, can be realised, in particular at elevated temperatures e.g. in the range of 50-100 °C.

In a preferred embodiment, the precipitation is carried out at a temperature in the range of 20-100 °C. Very good results have been achieved at a temperature in the range of 50-100 °C, in particular at a temperature in the range of 75-98 °C. The catalyst precursor may thereafter be isolated, e.g. by filtration, from the liquid and calcined, e.g. at a temperature of 200-750 °C for 1-5 hours. The catalyst may very suitably be activated by reduction with hydrogen, e.g. at a temperature of 250-600 °C, e.g. for 1-5 hours.

The catalyst may be coated with a protective layer, e.g. a fatty substance such as hardened soy bean fat, hardened palm oil fat, hardened sun flower oil fat or a combination thereof, which may serve to avoid oxidation of (parts of) the catalyst. This may for example be done by blending a (reduced) catalyst powder into the molten coating fat and subsequently solidifying the resulting suspension to form flakes or droplets of coated catalyst particles.

The nickel-, silica, alumina and magnesium sources may be chosen from sources commonly used to prepare catalysts.

Suitable nickel sources include inorganic nickel salts, preferably  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{NiCl}_2$ ,  $\text{NiSO}_4$ , and organic nickel salts, preferably nickel acetate. Preferably the nickel source is a solution or suspension of any of these salts.

Suitable silica sources include water glass, sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) and colloidal silica. Preferably the silica source is a solution or suspension of any of these components.

Suitable alumina sources include aluminium salts, preferably inorganic salts such as  $\text{AlCl}_3$ ,  $\text{Al}(\text{NO}_3)_3$  and sodium aluminate ( $\text{NaAlO}_2$ ). Preferably the alumina source is a solution or suspension of any of these salts.

5 Suitable magnesium sources include magnesium salts, preferably inorganic salts such as  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{MgCl}_2$ , and  $\text{MgSO}_4$ . Preferably the magnesium source is a solution or suspension of any of these salts.

A catalyst according to the present invention may be used for a variety of applications, and in particular for catalytic hydrogenation. The catalyst may be employed in a process for hydrogenating organic compounds  
10 wherein said compound is contacted with hydrogen in the presence of the catalyst. The process conditions may be chosen from the processes typically used for the hydrogenation of a particular compound. The process may be a batch or a continuous process.

An important advantage of a hydrogenation process according to the  
15 invention is the possibility to decrease the dosage of catalyst in order to achieve a particular conversion within the same hydrogenation time (contact time of feed (substrate) and catalyst) or to reduce the hydrogenation time at a particular catalyst dosage.

A process according to the invention has been found to be  
20 particularly suitable for the hydrogenation of a relatively clean oil (e.g. soy bean oil) and/or a more contaminated oil (e.g. fish oil or rape seed oil).

On the one hand it has been found possible to maintain a high activity in the presence of contaminations such as sulphur in the contaminated oil. On the other hand the selectivity has been found to remain high enough to  
25 achieve a favourable conversion of the unsaturated compounds. As a result the present invention also offers a considerable advantage since it offers the advantage that a single type of catalyst can very favourably be used in the hydrogenation of contaminated oil and also in the hydrogenation of clean oil. Thus a single stock of catalyst may be kept for the conversion of either of these  
30 products.



The invention will now be illustrated by the following examples.

### Example 1

5        A metal solution (1000 ml) containing 95 g Ni/l and 5g Mg/l was prepared from a  $\text{NiCl}_2$  solution (198 g Ni/l) and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . The base solution was prepared by dissolving 183 g  $\text{Na}_2\text{CO}_3$  and 44.4 g  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  in 1000 ml of demineralised water. The metal and base solution were injected at equal flow rates (1000 ml/hr) into a well stirred precipitation vessel containing 1725  
10 ml of demineralised water and 3.8 g of  $\text{Al}_2\text{O}_3$  as sodium aluminate. The temperature during precipitation was maintained at 95 °C while the pH was between 7.5 and 8.5.

After precipitation the precipitate was washed with demineralised water and dried overnight at 110 °C. The dried catalyst was calcined for 1.5 hours at  
15 375 °C and subsequently activated by reduction in hydrogen for 2 hours at 400 °C. The reduced catalyst powder was protected from air oxidation by dispersing it in an inert atmosphere in molten, hardened soybean fat at 80-100 °C. Catalyst flakes were formed by solidifying the blend of reduced catalyst powder and coating fat on a cooling plate. The catalyst properties of the  
20 calcined sample are as summarised in Table 1.

### Example 2

The catalyst of Example 2 was prepared according the procedure as  
25 described in Example 1, except that no magnesium was added.

### Example 3

The catalyst of Example 3 was prepared according the procedure as  
30 described in Example 1, except that no alumina was added.

### **Examples 4 and 5**

5       The catalysts of Examples 4 and 5 were prepared according to the  
procedure as described in Example 1, except that variations were made in the  
amount of starting materials resulting in catalyst properties as indicated in  
Table 1.

### **Examples 6 and 7**

10

The catalyst of Examples 6 and 7 were prepared according to the  
procedure as described with example 1, except that magnesium was replaced  
by copper and cobalt respectively.

### **15   Examples 8: Characterisation and performance of obtained catalysts**

The pore volume and BET surface area of the catalysts were measured  
by nitrogen adsorption/desorption using a Quantachrome Autosorb-6. Particle  
size was determined by laser diffraction using a Malvern Mastersizer 1002.  
20   The nickel surface area was measured by hydrogen chemisorption with a Carlo  
Erba Sorptometric 1900.

The soy bean oil (SBO) hydrogenating activity of the catalysts was  
determined by the hydrogenation of 500 g of soybean oil (iodine value 130) and  
measuring the time needed to reach an iodine value of 70. The catalyst loading  
25   was 0.0075% as nickel, the hydrogen pressure was 0.7 bar and the  
temperature was 204 °C. The iodine value was measured by the Wijs method  
as described in A.O.C.S. Official Method Cd 1-25 (1990).

The fish oil (FO) hydrogenation activity of the catalysts was determined  
by the hydrogenation of 500 g of fish oil (iodine value 160) at 180 °C, 2 bar  
30   hydrogen pressure and a nickel loading of 0.031%. The activity is expressed as

the time in minutes required to reach an iodine value (IV) of 115. The iodine value was measured by the Wijs method.

**Table 1: Properties of the calcined catalysts.**

5

	Example 1	Example 2	Example 3
Ni content (%)	58.5	62.3	76.2
Ni/Si atomic ratio	7.0	6.8	8.8
Ni/Al atomic ratio	20.1	19.7	-
Ni/Mg atomic ratio	10.1	-	13.7
Pore volume (ml/g cat)	0.57	0.65	0.44
BET area (m <sup>2</sup> /g cat)	377	375	385
Av. pore diameter (Å)	60	69	45
Particle size (µm)	6.8	6.8	13.4
Nickel surface area (m <sup>2</sup> /g Ni)	144	104	105
SBO hydrogenation activity (time to reach IV of 70)	23.5	31.5	58.5
FO hydrogenation activity (time to reach IV of 115)	23.5	31.0	44.5

Table 1 - continued.

	Example 4	Example 5
Ni content (%)	68.8	72.3
Ni/Si atomic ratio	5.5	20.1
Ni/Al atomic ratio	30.6	9.8
Ni/Mg atomic ratio	31.9	39.2
Pore volume (ml/g cat)	0.51	0.68
BET area (m <sup>2</sup> /g cat)	387	303
Av. pore diameter (Å)	53	90
Particle size (µm)	8.3	6.4
Nickel surface area (m <sup>2</sup> /g Ni)	109	101
SBO hydrogenation activity (time to reach IV of 70)	36.0	26.0
FO hydrogenation activity (time to reach IV of 115)	29.0	38.0

Table 1 - continued.

	Example 6	Example 7
Ni content (%)	58.3	58.3
Ni/Si atomic ratio	7.5	7.9
Ni/Al atomic ratio	18.0	18.8
Ni/Cu atomic ratio	9.7	-
Ni/Co atomic ratio	-	9.3
Pore volume (ml/g cat)	0.71	0.70
BET area (m <sup>2</sup> /g cat)	374	365
Av. pore diameter (Å)	75	76
Particle size (μm)	5.5	4.5
Nickel surface area (m <sup>2</sup> /g Ni)	72	97
SBO hydrogenation activity (time to reach IV of 70)		
FO hydrogenation activity (time to reach IV of 115)	83.5	100.0

Claims

1. Catalyst comprising nickel, silica, alumina and magnesium, wherein the nickel to silicium atomic ratio is 2 to 30, the nickel to aluminium atomic ratio is 9 to 40, and the nickel to magnesium atomic ratio is 5-75.
2. Catalyst according to claim 1, wherein the nickel to silicium atomic ratio is about 2-22, preferably about 2.5 to about 15.
3. Catalyst according to claim 1 or 2, wherein the nickel to aluminium atomic ratio is about 10-35, preferably about 15 to about 22.
4. Catalyst according to any of the claims 1-3, wherein the nickel to magnesium atomic ratio is about 5-50, preferably about 6 to about 20.
5. Catalyst according to any of the claims 1-4, wherein the catalyst is coated with a protective layer, effective in preventing oxidation of the catalyst, said protective layer preferably comprising a fatty substance.
6. Catalyst according to any of the claims 1-5, having pores, providing a pore volume ( $N_2$ , 20-600 Å) of 0.4 to 1 ml/g, preferably of 0.55 to 1 ml/g.
7. Catalyst according to any of the claims 1-6, having an average particle size of 3 to 8  $\mu m$ .

8. Catalyst according to any of the claims 1-7, having a nickel surface area of 75 to 200 m<sup>2</sup>/g.
9. Catalyst according to any of the claims 1-8, having a BET surface area of about 300 to about 450 m<sup>2</sup>/g.
10. Method for preparing a catalyst according to any of the preceding claims, wherein
- a nickel source, a silica source, an alumina source and a magnesium source are mixed in a liquid and co-precipitated therefrom to form a catalyst precursor,
  - the catalyst precursor is isolated from the solution, and
  - the catalyst precursor is activated to form the catalyst.
11. Method according to claim 10, wherein the catalyst precursor is activated by reducing at least part of the nickel content of the catalyst precursor, and optionally the catalyst precursor is calcined before being reduced.
12. Method according to claim 10 or 11, wherein the catalyst is coated with a protective layer.
13. Catalyst precursor obtainable in a method according to any of the claims 10-12.
14. Process for hydrogenating an unsaturated organic compound, wherein the unsaturated organic compound is contacted with hydrogen in the presence of a catalyst as defined in any of the claims 1-9 or 13.

15. Process according to claim 14, wherein the unsaturated organic compound is an unsaturated fatty substance.

16. Process according to claim 15, wherein the unsaturated fatty  
5 substance is a contaminated oil, a clean oil or a combination thereof.

17. Process according to claim 16, wherein the clean oil comprises a  
soybean oil, a sunflower oil, a palm oil, a cotton seed oil or a combination  
thereof.

10

18. Process according to claim 16, wherein the contaminated oil  
comprises fish oil, rape seed oil or a combination thereof.

19. Use of a catalyst according to any of the claims 1-10 in the  
15 hydrogenation of contaminated oil and clean oil.



Title: Nickel catalyst

Abstract

The present invention relates to a catalyst nickel, silica, alumina and magnesium, wherein the nickel to magnesium atomic ratio is 5-75.

In particular the present invention relates to a catalyst comprising nickel, silica, alumina and magnesium, wherein the nickel to silicium atomic ratio (Ni/Si) is 2 to 30 the nickel to aluminium atomic ratio (Ni/Al) is 9 to 40 and the nickel to magnesium atomic ratio (Ni/Mg) is 5-75.

The invention further relates to a method for preparing such a catalyst.

The invention further relates to a process for hydrogenating unsaturated organic compounds.